Influence of Ammonia Contamination on HT-PEM Fuel Cell Platinum Catalyst

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PRiME 2020, I01D-2339, 08.10.20

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Outline

- Introduction of the Group
- Motivation & Projects Goals
- Contamination in Fuel Cell: Sources and Species
- Strategies & Experiments
- MEA Characterization
- RRDE Measurements
- Summary

Research on Fuel Cells

- DLR Institute of Networked Energy Systems
  - Development of technologies and concepts for energy supply based on renewables
  - Department Fuel Cells

- DLR Institute of Engineering Thermodynamics
  - Research into the field of efficient energy storage systems
  - Department Electrochemical Energy Technology

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in progress

The group <u>Characterisation</u> merges into the group <u>HT-PEM</u>.

- *Investigation of aging processes in (LT- and HT-PEM) fuel cells and development of cell components.*
- *Bipolar plates, membranes, catalysts, electrodes, membrane electrode assemblies, single cells and short stacks.*

Project „HAlMa“

H_2 and Cations-Contamination: Aging-Effects, Material and Sensor Development

Investigation of the Influence of the H_2 Impurities and Corrosion Products on the Catalyst Layer

Development of Stable Membrane

Development of the Monitoring Sensor System Detecting H_2 Quality at a Gas Station

Project duration:
01.12.16 – 30.06.20

Funding number:
03ET6098D

Fraunhofer ISE

HYDAC

DLR Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center
Institute of Networked Energy Systems

ZeMA Zentrum für Mechatronik und Automatisierungstechnik

fumatech Funktionelle Membranen und Anlagentechnologie

Supported by:
Federal Ministry for Economic Affairs and Energy
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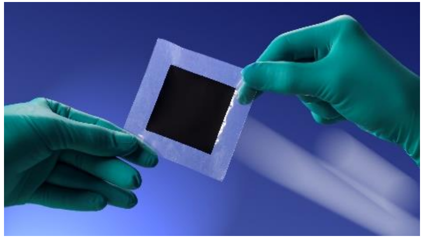
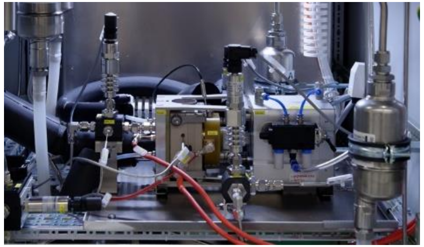
Project „HT-Kathodenluft II“



Membrane Electrode Assembly
Foto: DLR



Single Cell Test Station
Foto: DLR

Impact of Air Impurities on HT-PEM Fuel Cell Operation

Development of Operation Matrix
Evaluation of Scenarios with Pollutants

Impurity Impact on Fuel Cell Components
Electrochemical Study of Degradation

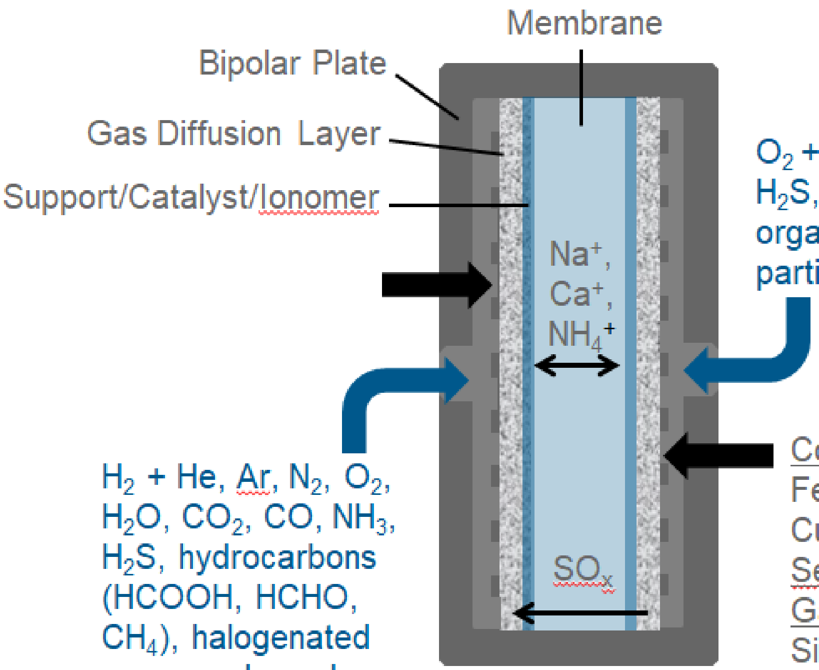
Development of Recovery Strategies

Project duration:
01.01.18 – 30.09.20

Funding number:
19815N

Supported by:
Federal Ministry of Economics and Technology
on the basis of a decision by the German Bundestag

Contaminations in Fuel Cells: Sources and Species



O_2 + N_2, CO_2, CO, SO_x, H_2S, NO_x, NH_3, O_3, organic compounds and particles

H_2 + He, Ar, N_2, O_2, H_2O, CO_2, CO, NH_3, H_2S, hydrocarbons (HCOOH, HCHO, CH_4), halogenated compounds and particles

Corrosion:
Fe^{3+}, Cr^{3+}, Mn^{x+}, Ni^{2+}, Cu^{2+}, Ba^{2+}, Al^{3+}

Sealings/Humidification/ Gases:
Si^{x+}, Al^{3+}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{x+}, Cu^{2+}, V^{x+}, Cr^{3+}

Ammonia contaminations

- Enter the fuel cell via cathode as well as anode gas stream
- Effect on the ionomer and electrolyte
- Harmful impact on ORR

Electrochemical investigation of the HT-PEMFC single cell and the platinum catalyst in the presence of ammonia

Strategies & Experiments

Test bench / MEA

MEA
APM-25 / Advent Technologies SA

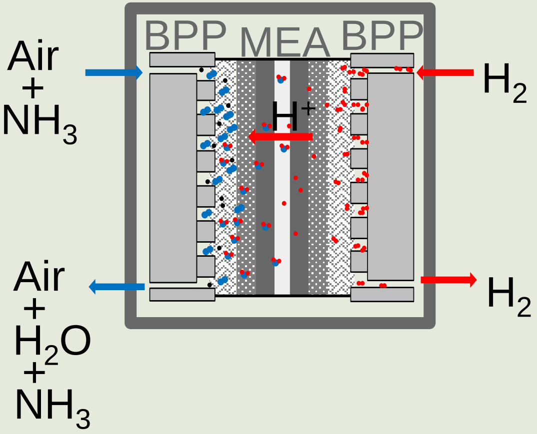
Harmful gas
10 ppm NH_3 in cathode air stream

Test time
500 h

Temperature
160 °C

Current density
300 $mAcm^{-2}$

Stoichiometry
1.5/2.0 (H_2/Air)



RRDE / Catalyst

Catalyst
Pt/C HiSPEC 9100

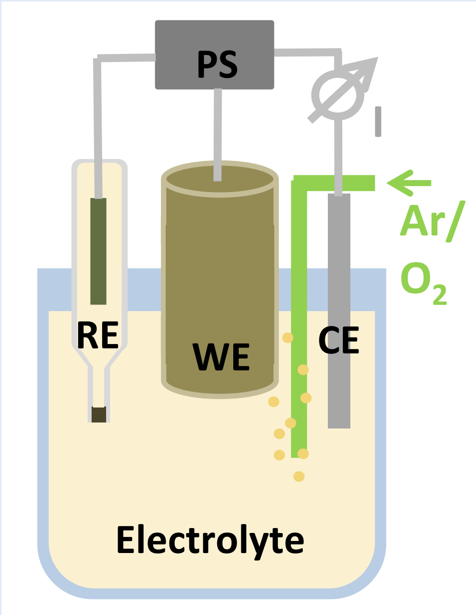
Electrolyte
0.5 M H_3PO_4

Contaminant
10 and 100 ppm of $NH_4H_2PO_4$

Working electrode
Glassy carbon coated with Pt/C

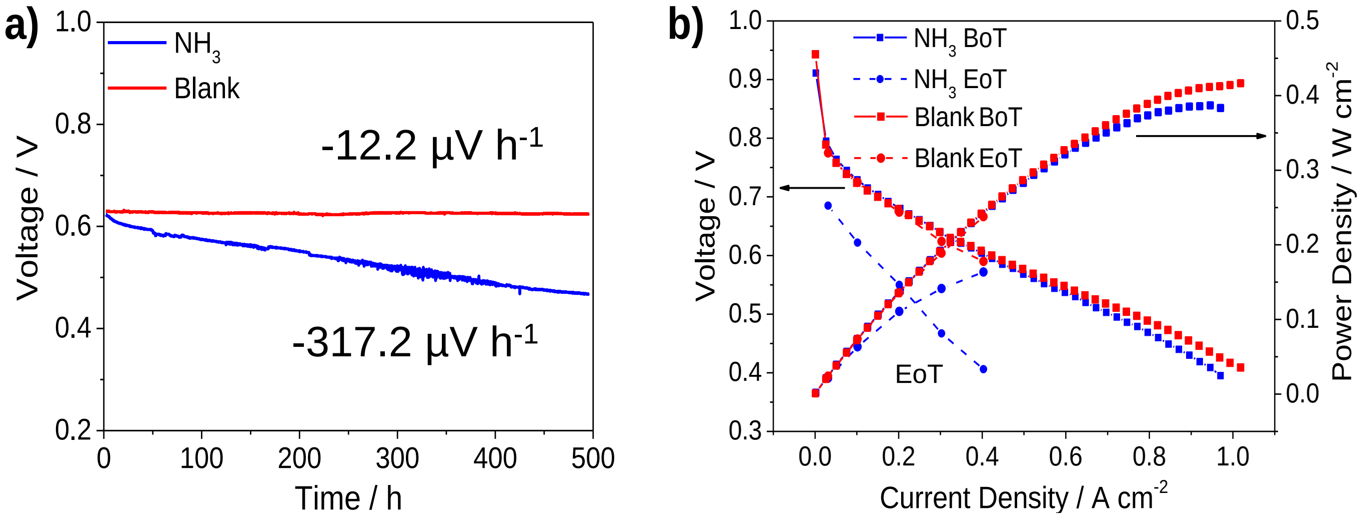
Counter electrode
Pt wire

Reference electrode
Hg/$HgSO_4$



MEA under HT-PEMFC conditions

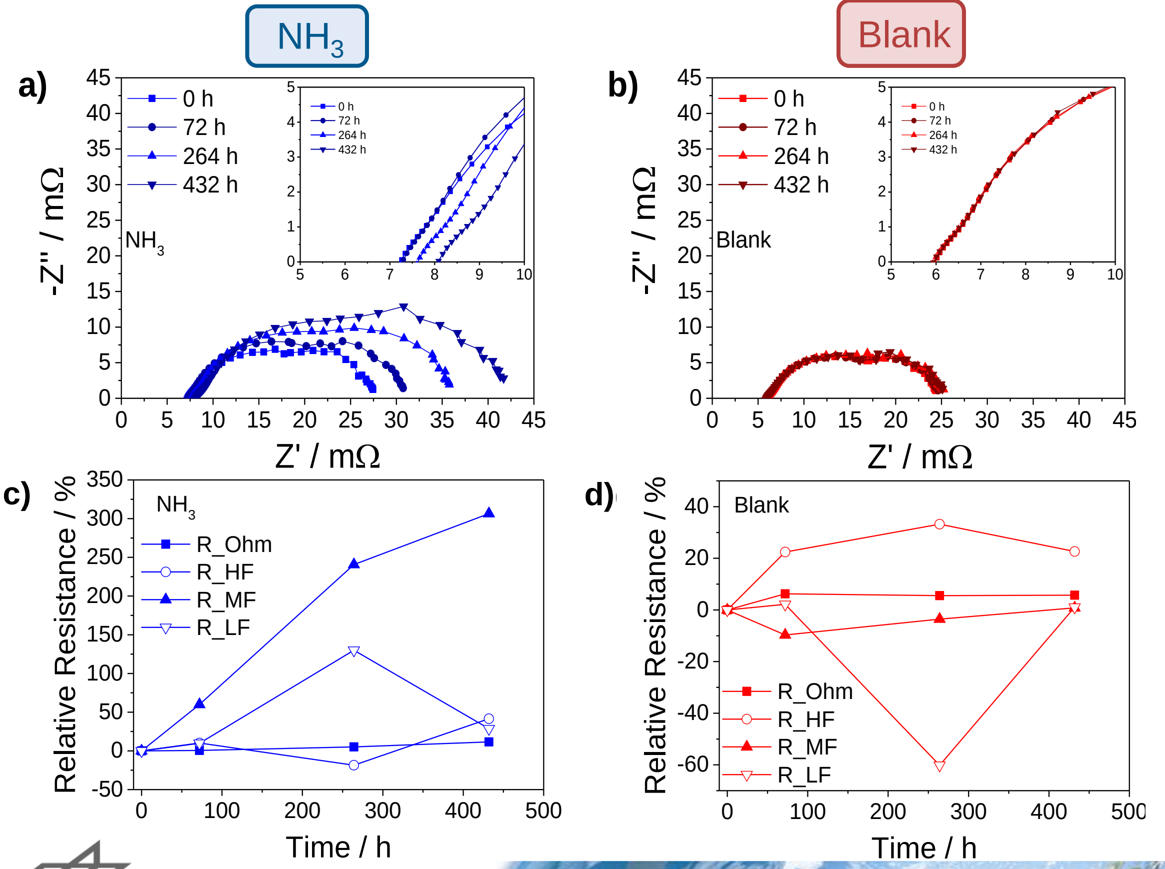
Temperature: 160 °C | Current density: 300 mAcm^{-2} | Stoichiometry: 1.5/2.0 (H_2/Air)



Higher degradation rate and cell performance losses in the presence of contaminant due to chemical reaction of NH_3 with H^+ inside the membrane and catalytic layers

a) cell voltage response over time of cell operation and b) polarisation curves measured at BoT and EoT, where EoT is a quasi polarization curve measured at 0.03, 0.1, 0.2, 0.3, 0.4 A cm^{-2}

Nyquist Plots and Relative Resistances of MEAs



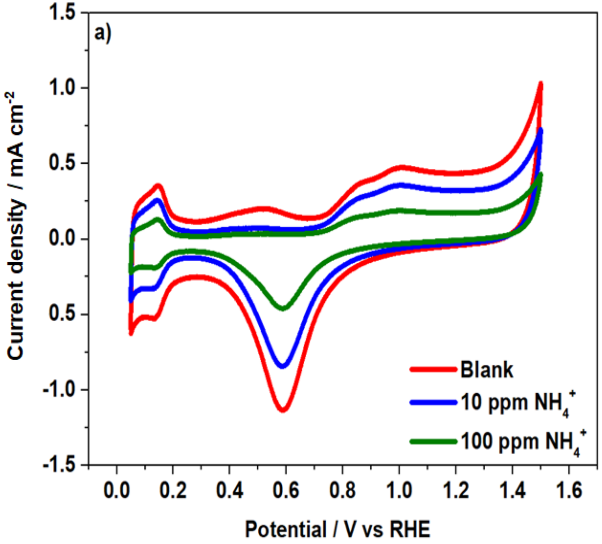
Increased polarisation, ohmic, charge and mass transfer resistances during "NH_3" operation

Significant degradation of the anode and cathode as well as the electrolyte membrane

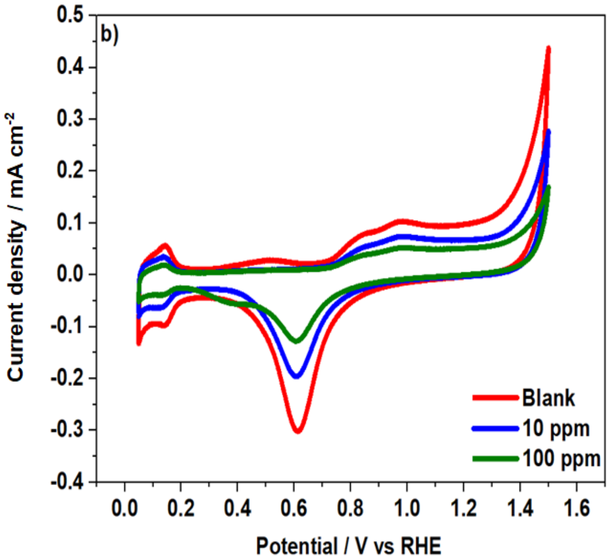
RRDE Experiments. Electrochemical Surface Area Determination

Pt/C Catalyst | 0.5 M H_3PO_4 | 10 and 100 ppm of NH_4^+

50 mV s^{-1}



10 mV s^{-1}

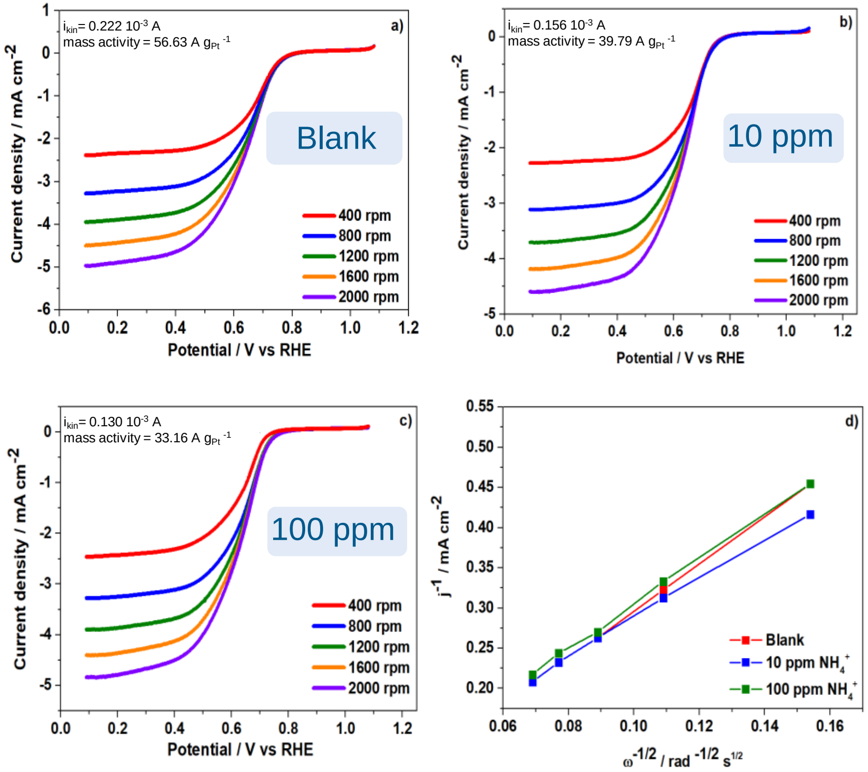


$$ECSA_{H2} = Q_H / \nu \cdot \rho \cdot L_{Pt}$$

where ν is scan rate,
ρ is the charge density of hydrogen oxidation in presence of one Pt atom,
L_{Pt} is the mass of Pt.

Sample	ECSA, $m^2 g_{Pt}^{-1}$
Blank	48
10 ppm NH_4^+	27
100 ppm NH_4^+	18

ORR experiments



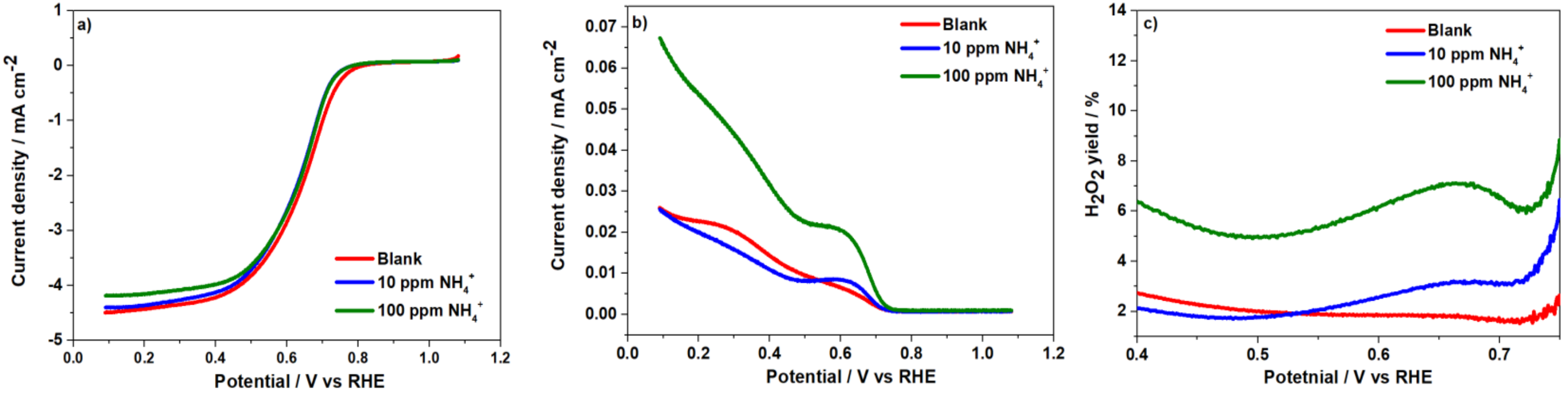
Koutecky-Levich analysis

- first order kinetics with respect to O_2
- complete 4-electron reduction of O_2 to water

$$\text{slope} = (0.62nFD_O^{2/3}\nu^{-1/6}C_O)^{-1}$$

where F is Faraday's constant,
D_O is the diffusivity of O_2 molecule in the electrolyte,
v is the kinematic viscosity,
C_O is the concentration of O_2 in the electrolyte.

H_2O_2 formation mechanism



(a) ORR curves of the Pt/C catalyst in the absence of NH_4^+ and in the presence of 10 ppm and 100 ppm NH_4^+ in the cathodic scan at 1600 rpm and 10 mV s^{-1}; (b) H_2O_2 formation current during ORR reaction in O_2-saturated 0.5 mol L^{-1} H_3PO_4 at 1600 rpm, (c) relative yield of H_2O_2 in the ORR.

Increased H_2O_2 formation in the presence of 100 ppm NH_4^+

Kinetic Parameters of the catalyst

Sample	ECSA, $m^2 g_{Pt}^{-1}$	Kinetic Current at 0.70 V vs RHE, mA	Mass Activity, mA g_{Pt}^{-1}	Specific Activity, mA cm^{-2}
Blank	48	0.222	56.63	4.6
10 ppm NH_4^+	27	0.156	39.79	5.7
100 ppm NH_4^+	18	0.130	33.16	7.2

- Lower ECSA
- Reduced kinetic current
- Decreased mass activity

Significant degradation of catalyst performance in the presence of ammonia

Summary

- HT-PEM fuel cell performance degradation equal to -317.2 µV h^{-1} during cell operation with poisoned cathode air
- enlarged charge transfer resistances of both electrodes and a highly affected membrane in the presence of NH_3
- reduced ECSA and mass activity of ORR catalyst in the presence of 10 and 100 ppm during RRDE experiments
- ammonium species adsorption on Pt leads to a reduction in active sites and causes changes in the kinetic parameters or the reaction mechanisms of the ORR

Thank you for your attention!

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